

OPTION A: ANALYTICAL CHEM

A8 – VISIBLE AND ULTRAVIOLET (UV-VIS) SPECTROSCOPY

IB Chemistry

TAD07

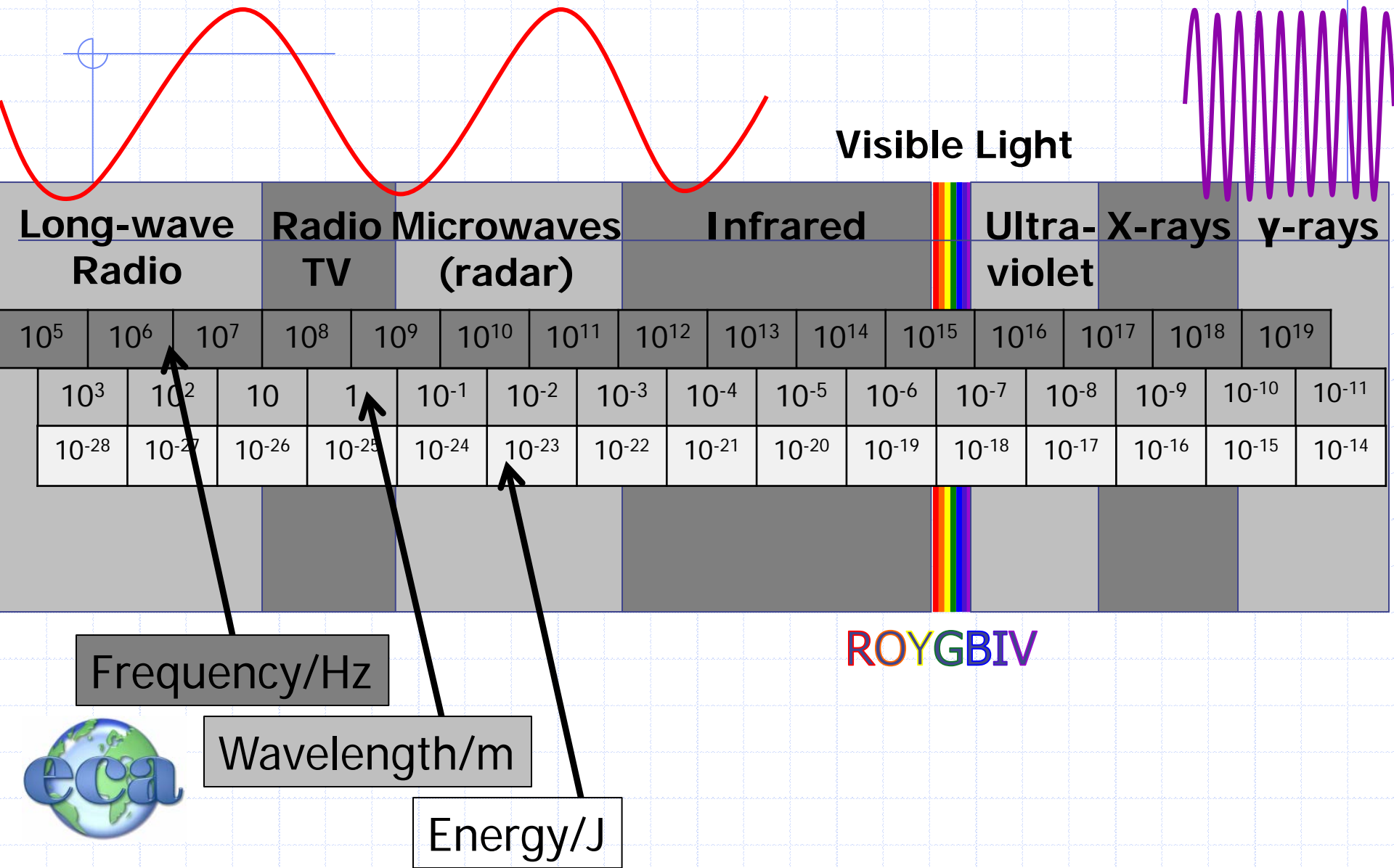


A8 - Visible and ultraviolet (UV-Vis) spectroscopy

- A.8.1 Describe the effect of different ligands on the splitting of the d orbitals in transition metal complexes. (2)
 - *The ligands should include NH_3 , H_2O and Cl^- .*
- A.8.2 Describe the factors that affect the color of transition metal complexes. (2)
 - *Include the identity of the metal ion (for example, Mn^{2+} or Fe^{2+}), the oxidation number of the metal (for example, for Fe, +2 or +3) and the identity of the ligand (for example, NH_3 or H_2O). These factors will be assessed only for octahedral complexes in aqueous solution.*
- A.8.3 State that organic molecules containing a double bond absorb UV radiation. (1)
 - *Refer to conjugated and delocalized systems, including arenes, alkenes and chlorophyll.*
- A.8.4 Describe the effect of the conjugation of double bonds in organic molecules on the wavelength of the absorbed light. (2)
 - *Examples should include retinol and phenolphthalein. Aim 8: The application of this in sun creams could be discussed.*
- A.8.5 Predict whether or not a particular molecule will absorb UV or visible radiation.
- A.8.6 Determine the concentration of a solution from a calibration curve using the Beer-Lambert law. (3)



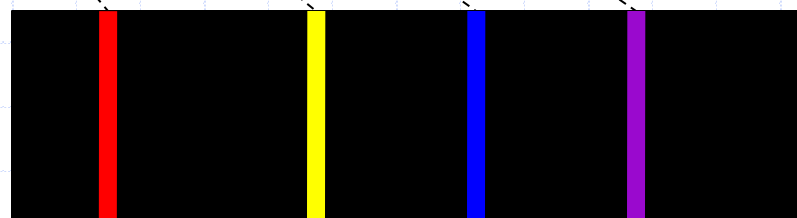
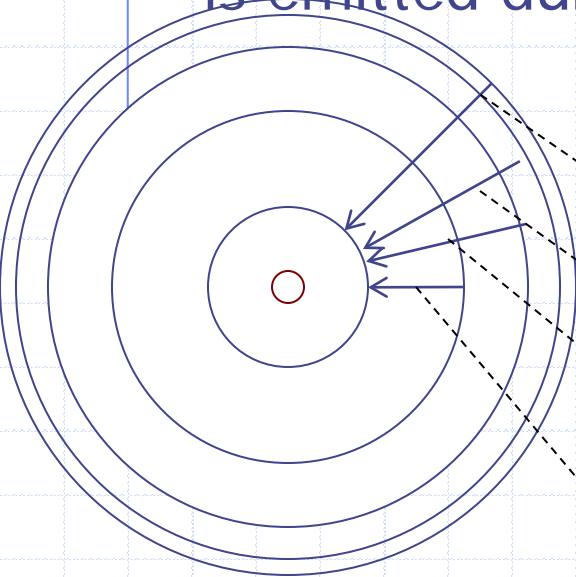
2.3.1 – Electromagnetic Spectrum



2.3.3 – Electron Emission Energy

- The difference in energy levels as electrons move corresponds to the energy of the wavelength of light that is emitted during the process

- The difference in energy level is also known as “**quanta**” which is where the term quantum theory derives itself



3→2

4→2

5→2

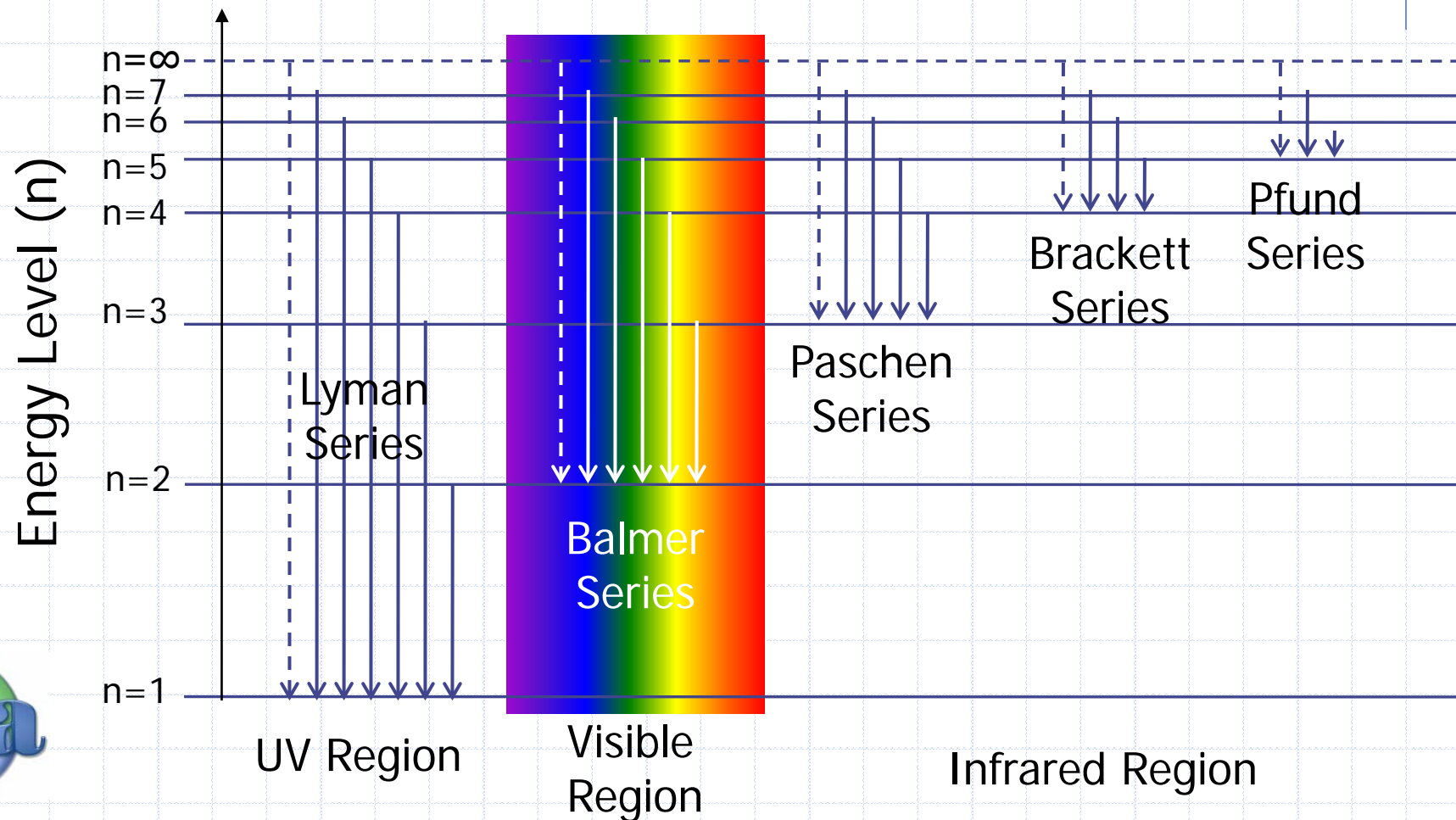
6→2

**This diagram is an over-simplification of what occurs from level to level. The concept and trend holds true, the specifics about colors do not necessarily*



2.3.3 – Hydrogen Emission

The origin of each of hydrogen's emissions can be summarized through the following diagram



What we see:

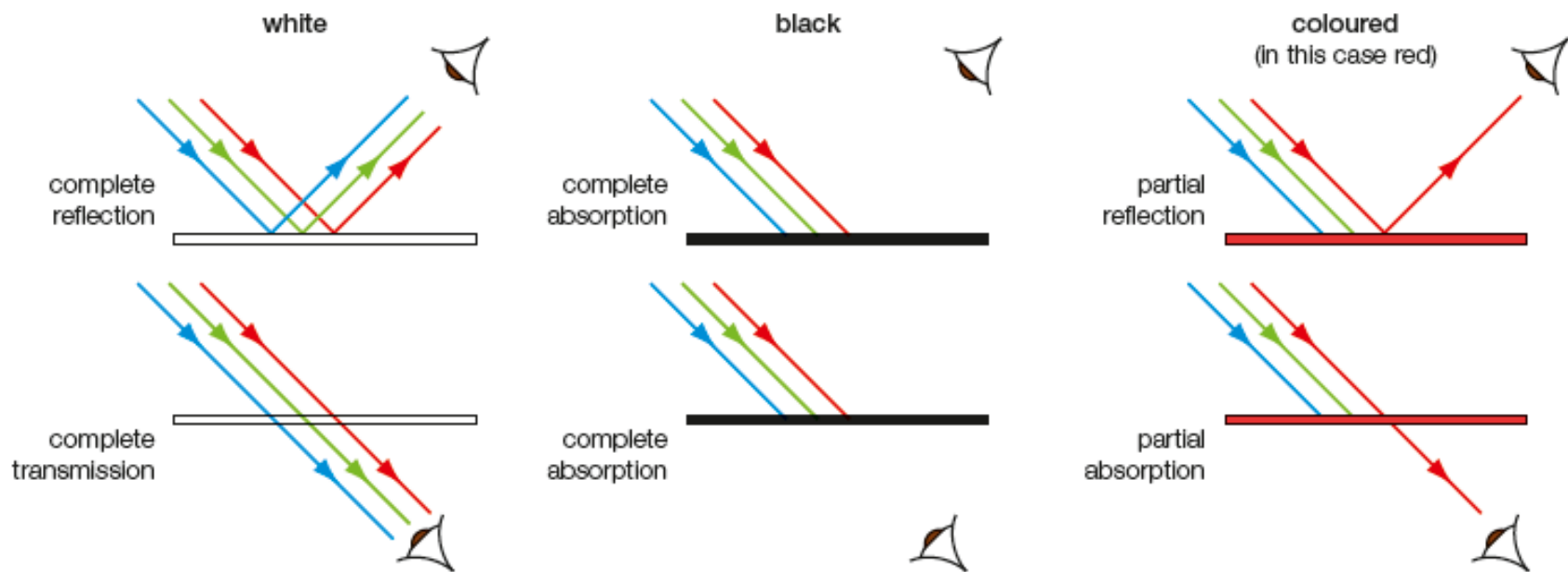


Figure 21.89 Colour and absorption of visible light wavelengths

Complementary Colors

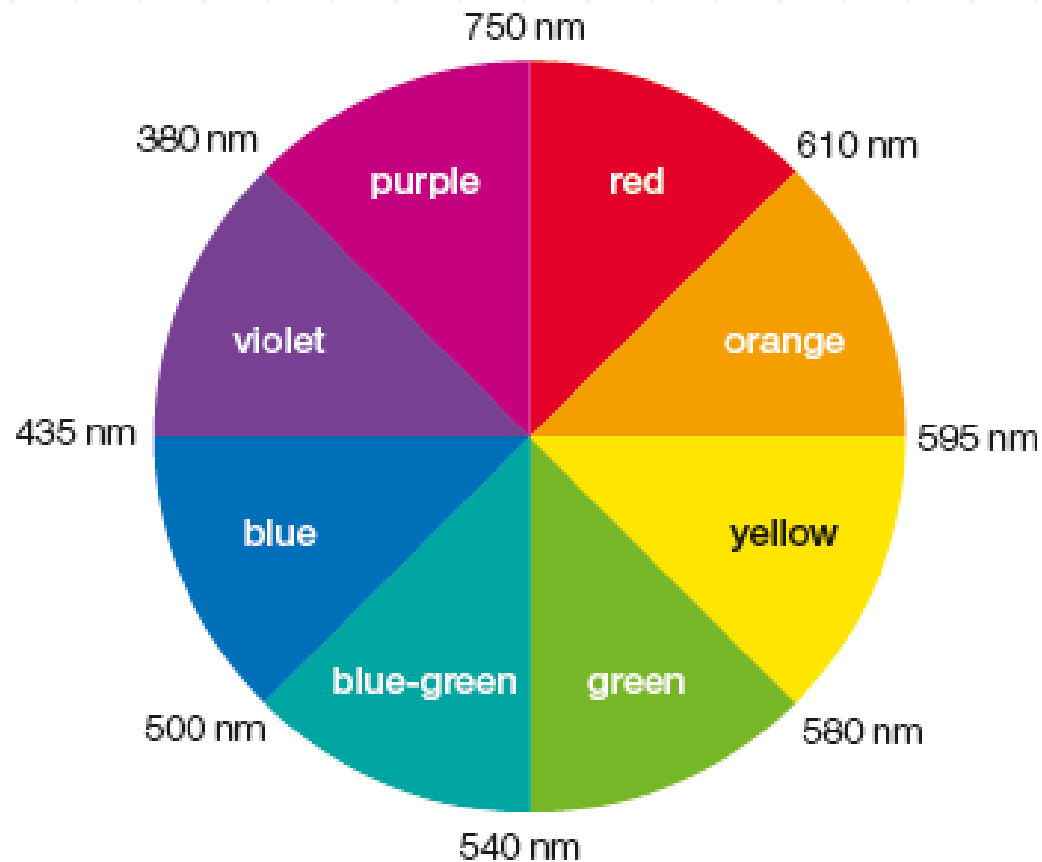


Figure 21.90 A simple colour wheel: complementary colours are opposite one another



Absorption of Light

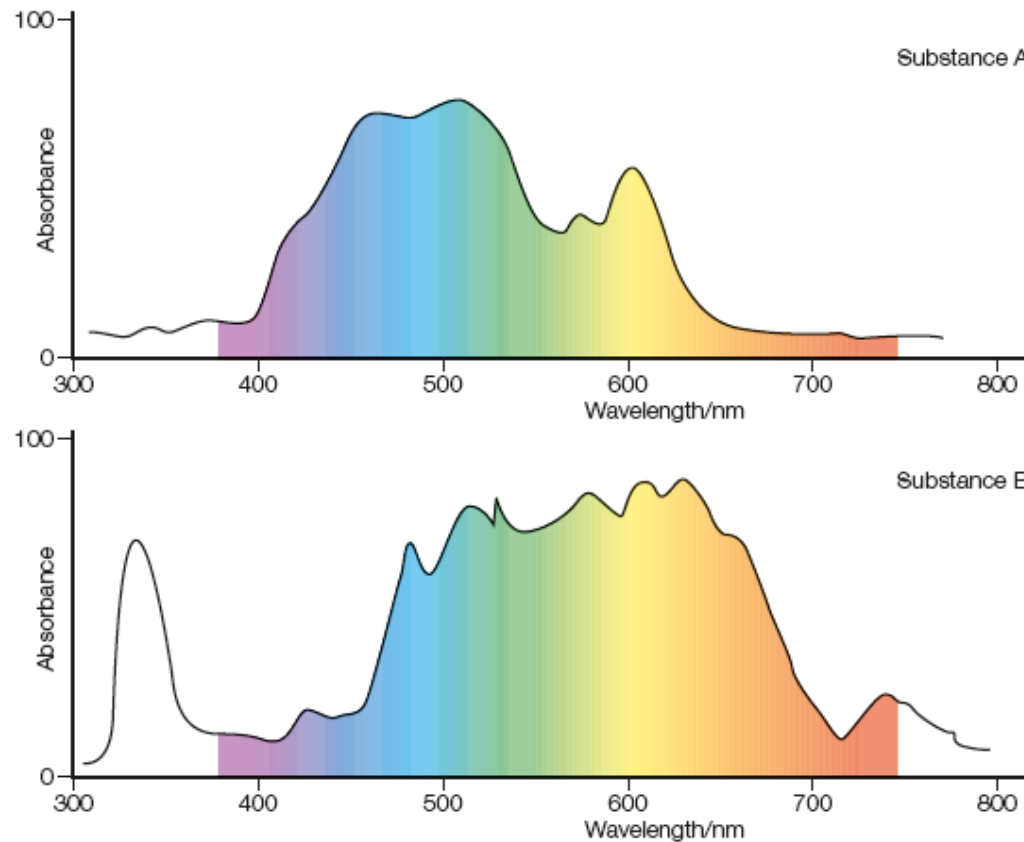


Figure 21.91 Absorption spectra for substances A and B



A.8.1 Describe the effect of different ligands on the splitting of the d orbitals in transition metal complexes. (2)

- Refer to topics 13&14 (HL Periodicity and Bonding) for further review on d-orbital splitting
- Transition metals form “complexes” in which coordinate covalent (dative) bonds are formed with nucleophilic ligands
 - Common Ligands
 - Halides, OH^- , H_2O , NH_3 , CN^- , CO
 - Ex: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$, $[\text{Fe}(\text{CN})_6]^{3-}$
- Transition metals that are NOT colored
 - Zinc – completely full 3d subshell ($3d^{10}$)
 - Scandium – empty 3d subshell ($3d^0$)



Ligands

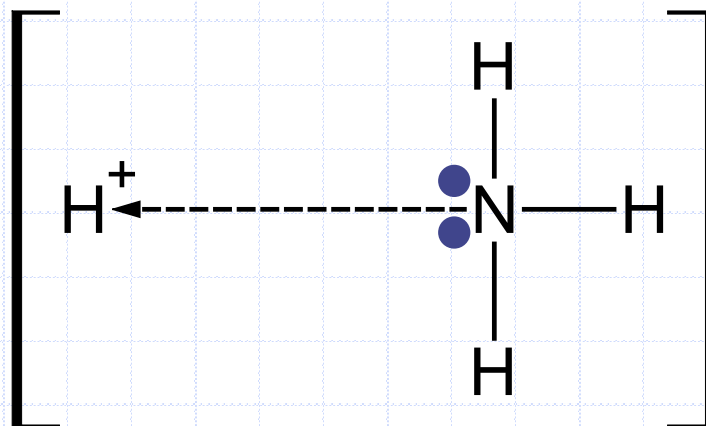
13.2.4 Define the term ligand. (1)

- A d-block metal **complex-ion** consists of a d-block metal ion surrounded by a definite number of ligands.
 - **Ligands** are molecules or negative ions with lone pairs of electrons
 - Common ligands are: H_2O , NH_3 , Cl^- , OH^- , CN^-
 - Also known as nucleophiles as they are attracted to the positive charge of a nucleus (in this case the effective nuclear charge of a transition metal ion).
 - Ligands share their lone pair with the empty orbitals in the central d-block
 - The ligands behave as Lewis Bases (e^- pair donors – Topic 08/18)



Coordinate Covalent Bonds

- When both electrons that are shared (in a single bond) come from the same atom, the bond is known as a **coordinate bond** or a **dative bond**.
 - Shown as an arrow (\rightarrow) instead of a bond (-) where the electrons came from the source of the arrow
 - The **coordination number** is the number of bonds (to **ligands**) formed around the central atom
 - In Topic 08 (Acids and Bases) known as **Lewis acids and bases**

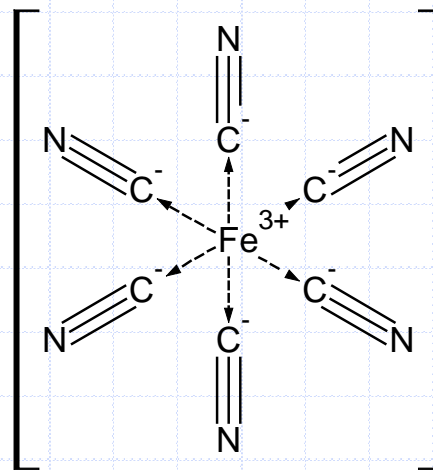


Formation of Complex Ion Compounds

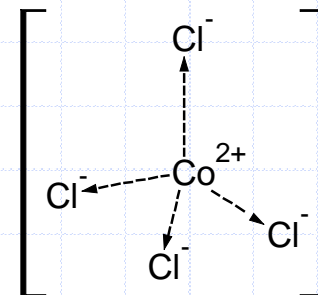
13.2.5 Describe and explain the formation of complexes of d-block elements.

- The coordination number is simply the number of ligands attached to the ion:

- $[\text{Fe}(\text{CN})_6]^{3-}$ coordination of 6
- $[\text{Co}(\text{Cl})_4]^{2-}$ coordination of 4



Note: arrow are backwards



- Each of the resultant complex ions will pick up a charged particle to form a neutral salt
 - If the ligand is charged, the species becomes more negative and must pick up another cation (metal)
 - If the ligand is neutral, the species remains positive and must pick up an anion (non-metal)



Electron Configuration of Neutral T-metals

El.	#	Noble Not.		3d					4s
Sc	21	[Ar]3d ¹ 4s ²	[Ar]	↑					↑ ↓
Ti	22	[Ar]3d ² 4s ²	[Ar]	↑	↑				↑ ↓
V	23	[Ar]3d ³ 4s ²	[Ar]	↑	↑	↑			↑ ↓
Cr	24	[Ar]3d ⁵ 4s ¹	[Ar]	↑	↑	↑	↑	↑	↑
Mn	25	[Ar]3d ⁵ 4s ²	[Ar]	↑	↑	↑	↑	↑	↑ ↓
Fe	26	[Ar]3d ⁶ 4s ²	[Ar]	↑ ↓	↑	↑	↑	↑	↑ ↓
Co	27	[Ar]3d ⁷ 4s ²	[Ar]	↑ ↓	↑ ↓	↑	↑	↑	↑ ↓
Ni	28	[Ar]3d ⁸ 4s ²	[Ar]	↑ ↓	↑ ↓	↑ ↓	↑	↑	↑ ↓
Cu	29	[Ar]3d ¹⁰ 4s ¹	[Ar]	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑
Zn	30	[Ar]3d ¹⁰ 4s ²	[Ar]	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓

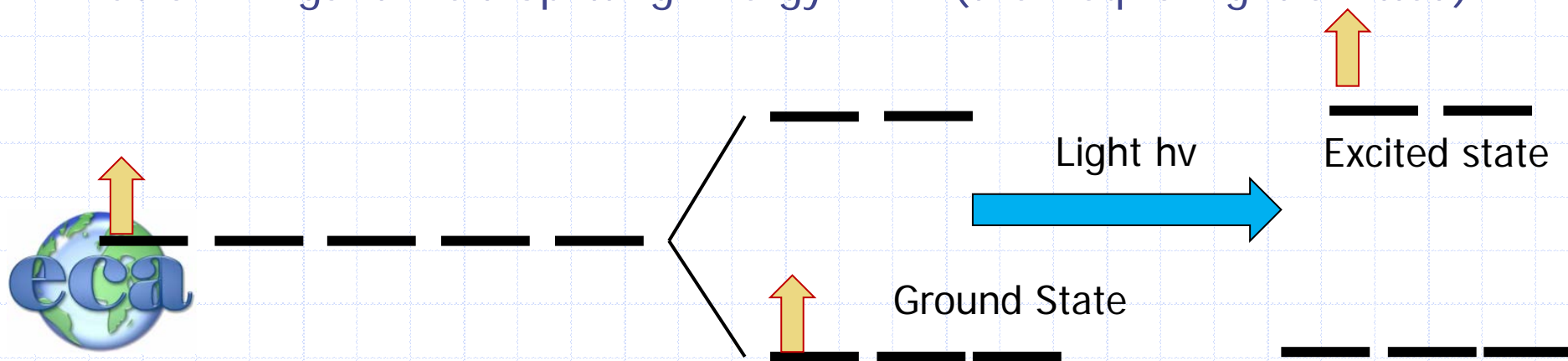
Electron Configuration of Charged T-metals

El.	#	Noble Not.		3d					4s
Sc ³⁺	21	[Ar]	[Ar]						
Ti ²⁺	22	[Ar]	[Ar]	↑	↑				
V ²⁺	23	[Ar]3d ³	[Ar]	↑	↑	↑			
Cr ³⁺	24	[Ar]3d ³	[Ar]	↑	↑	↑			
Mn ²⁺	25	[Ar]3d ⁵	[Ar]	↑	↑	↑	↑	↑	
Fe ²⁺	26	[Ar]3d ⁶	[Ar]	↑↓	↑	↑	↑	↑	
Co ²⁺	27	[Ar]3d ⁷	[Ar]	↑↓	↑↓	↑	↑	↑	
Ni ²⁺	28	[Ar]3d ⁸	[Ar]	↑↓	↑↓	↑↓	↑	↑	
Cu ²⁺	29	[Ar]3d ⁹	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	
Zn ²⁺	30	[Ar]3d ¹⁰	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	

Colored Compounds

13.2.6 Explain why some complexes of d-block elements are colored. (3)

- Most d-block metal compounds are colored, both in solution and in the solid state.
- The colors are due to the presence of incompletely filled 3d sub-shells
- In an isolated gaseous d-block metal, the five 3d subshells are of equal energy and different orientations
- In a complex ion, the 3d sub-shells are oriented relative to the ligands – those close to the ligand experience repulsion and are raised in energy
- This 3d sub-shell is split into two energy levels
- Color = Ligand Field Splitting Energy = ΔE (the freq. of light emitted)



Relative Splitting Energies

- Orbital Splitting Power:
 - $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^- < CO$
- $[Cu(H_2O)_6]^{2+} (aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O$
Blue Green/Yellow
 - Energy: Blue > Green/Yellow
 - Ligand Field Splitting: Decreased
 - Ligand: Cl^- causes weaker splitting than H_2O
 - Coordination: Less ligands (4 vs 6) causing repulsions



UV Absorption

A.8.3 State that organic molecules containing a double bond absorb UV radiation. (1)

- Compounds that absorb UV light:
 - Molecules containing **double bonds**
 - C=C (Alkenes, arenes)
 - C=O (Aldehydes, ketones, carboxylic acids, etc)
 - Molecules with conjugated systems
 - Alternating C-C and C=C bonds like benzene
 - Called delocalized systems due to the resonance
 - Many biological molecules (chlorophyll, beta-carotene, hemoglobin, retinol, etc)
 - Dyes
 - Indicators (like phenolphthalein)

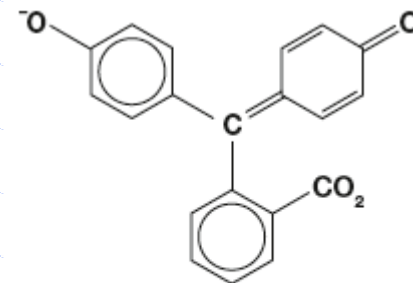


Figure 21.108 Structure of the alkaline form of phenolphthalein

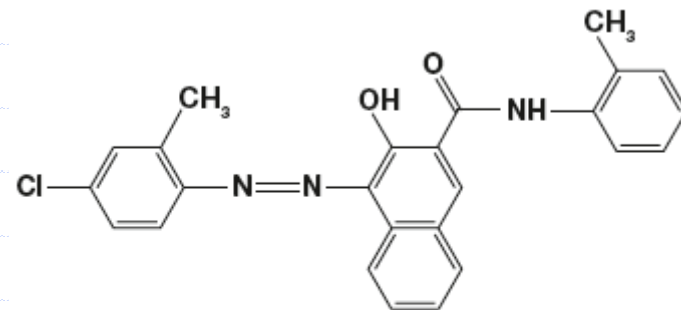


Figure 21.107 Structure of a red azo dye



UV Spectra Prep

- State of Material:
 - Recorded in solution
 - Water – H_2O
 - Ethanol – $\text{CH}_3\text{CH}_2\text{OH}$
 - Methanol – CH_3OH
 - ~~Benzene~~ – contains double bonds
 - Transparent solids and gases (if contained) can be used as well.
- Sample is added to a cuvette in the case of a liquid/aqueous sample
- A specific wavelength λ of energy is sent through a sample
 - Intensity I_N is measured
 - Intensity I_{OUT} is measured
- Intensities are compared and result in an absorbance at that frequency
- Other wavelengths are scanned if appropriate
- The absorbance must then fit into a calibration curve (made by standard solutions of known concentrations) to provide results.



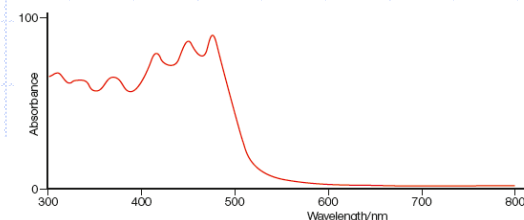
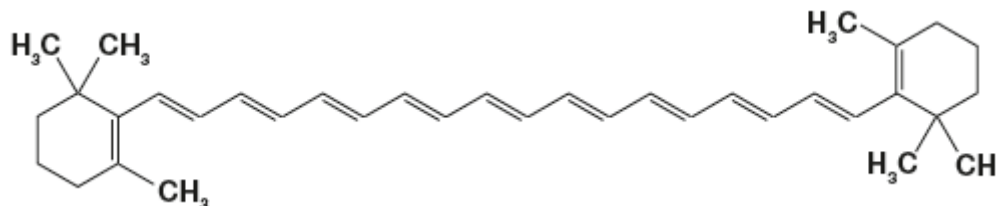
Conjugation Effect

A.8.4 Describe the effect of the conjugation of double bonds in organic molecules on the wavelength of the absorbed light. (2)

- The more conjugated (longer C-C=C-C=C) the molecule the more delocalized the molecule becomes and absorption peaks move to a lower energy (higher wavelength)

Name of Molecule	Structure of Molecule	λ_{\max}
Ethene	$\text{CH}_2=\text{CH}_2$	171
Buta-1,3-diene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	217
Hexa-1,3,5-triene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	258

- If the conjugation is incredibly long, the UV radiation will be shifted so much that the compound may even appear in the visible region and appear colored
 - For example beta-carotene

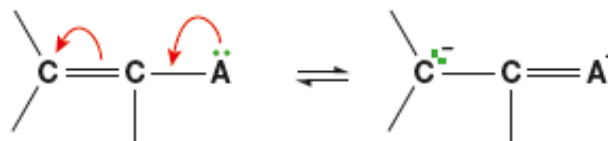


Molecules that absorb UV

A.8.5 Predict whether or not a particular molecule will absorb UV or visible radiation.

- Molecules likely to absorb UV light:
 - Those that are conjugated
 - Most common = alternating C-C and C=C
 - The conjugation enhances the presence of functional groups with lone pairs which would extend conjugation even further

Figure 21.123 Resonance interaction of a lone pair with double bonds to increase the extent of conjugation



- Molecules that give UV and visible (conjugation affected)

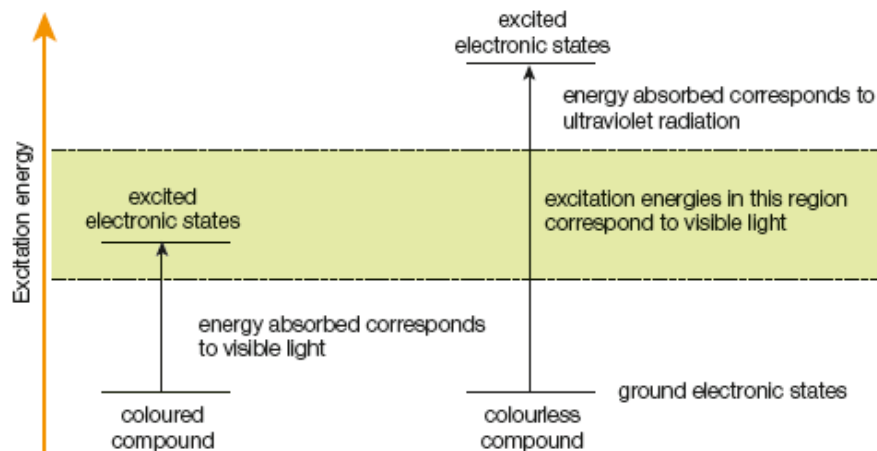


Figure 21.124 The energy needed to excite an electron in a coloured molecular substance and in a colourless molecular substance



Beer's Law

A.8.6 Determine the concentration of a solution from a calibration curve using the Beer–Lambert law.(3)

- Luckily, we studied this extensively last year.
- Can be related to Atomic Absorption in that it needs to have a standardized set of solutions for comparison
- Absorbance, $A = \log_{10} \frac{Intensity_{IN}}{Intensity_{OUT}}$
 - $A = 0$ means no radiation has been absorbed
 - $A = 1$ means 90% of the radiation has been absorbed
 - $A = \log_{10} \frac{100}{10} = \log_{10}(10) = 1$
 - Depends on how many molecules the radiation comes in contact with
 - High [conc] = high A
 - Low [conc] = low A
 - Decreases exponentially with the path length
 - Thin container (high path length) = low A
 - Thick Container (low path length) = high A



Beer-Lambert Law

■ The Beer-Lambert Law

- $A = \log_{10} \frac{\text{Intensity } IN}{\text{Intensity } OUT} = \epsilon c l$
 - ϵ = molar absorptivity coefficient ($\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)
 - c = concentration (mol dm^{-3})
 - l = path length (cm)
- The absorbance is directly proportional to the concentration and path length of the sample
- The molar absorption coefficient is a number characteristic to the specific molecule absorbing the radiation.



Data Extrapolation

- In order to run a sample, you must first set up a calibration curve based on standard (known to a certain degree) solutions:

Absorbance	0.27	0.54	0.82	1.08	1.35
Concentration (mol dm ⁻³)	0.010	0.020	0.030	0.040	0.050

Table 21.10 Concentrations and absorbance values

- Now that we have a curve:
 - Unknown samples can be added to the spectrometer which result in an absorbance reading
 - You can use the equation for the line or the graph and linear digression to determine the concentration.

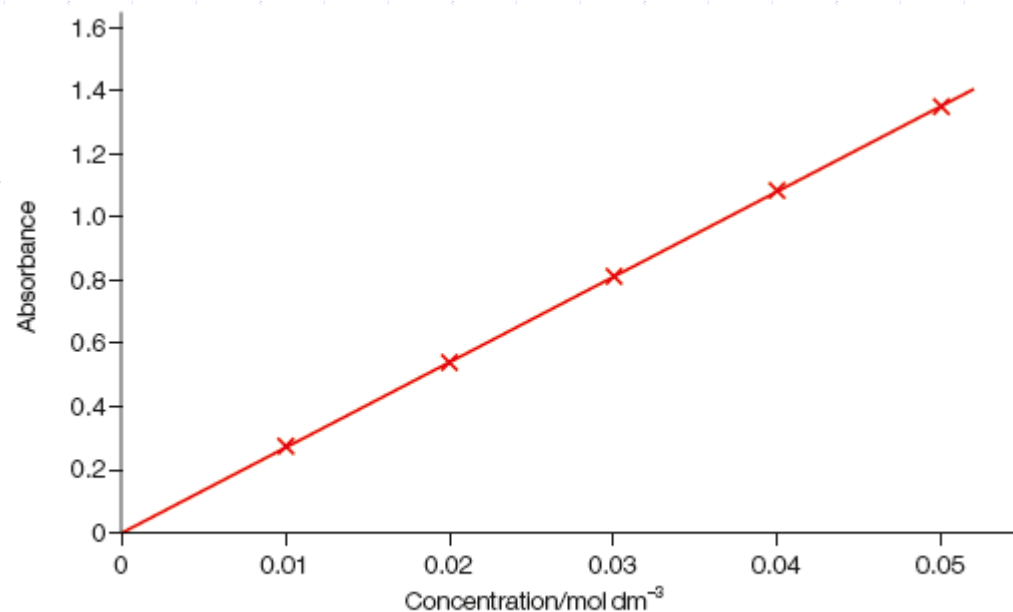


Figure 21.131 Absorbance versus concentration for substance X

